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BY

MARION THOMAS O'SHAUGHNESSY, JR.

A.B., University of Florida, 1934

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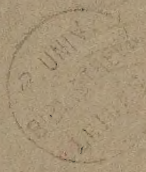

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1940

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ACKNOWLEDGMENTS

The author wishes to express his appreciation to Professor W. H. Rodebush for making possible this investigation. He wishes to thank also Professor Roger Adams for the suggestion of certain biphenyl compounds for study and for advice as to their preparation, Professor R. S. Mulliken of the University of Chicago for very helpful conversations with regard to the application of the ideas developed in his papers on the intensities of molecular spectra, Messrs. N. Kornblum, C. H. McKeever, E. C. Horning and S. L. Scott for samples of pure compounds for investigation, and Miss Barbara Williamson for assistance with some of the measurements.

THEORETICAL

The four electrons of the L shell of doubly bonded carbon occupy three s bonding orbitals of mixed 2s, $2p_x$ and $2p_y$ character, with their axes of symmetry in the same plane, and one π bonding orbital, the $2p_z$ orbital of the atom, with axis perpendicular to the plane. The additional energy of a double bond arises from the interaction of π electrons, with paired spins, on adjacent atoms. When a series of double bonds is conjugated each atom along the chain or ring possesses a π electron, and other patterns of pairing and interaction besides that normally assumed will exist and will lower the energy of the system through resonance. For bonding, however, π orbitals must have parallel or nearly parallel axes, so that for maximum conjugation complete coplanarity of the double bond system (parallel orientation of all the π orbitals) is required. If two adjacent double bonds in a chain are turned from coplanarity through a large angle, the chain is effectively divided into two smaller conjugated systems with slight interaction upon one another.

Mulliken has shown recently[1] that the intense long wave-length absorption bands of neutral conjugated molecules are due to transitions from a non-ionic ground state to an ionic excited state with positive and negative charges (no π electron and two π electrons, respectively) at the opposite ends of the system. The ionic form requires rearrangement of the bonding between the atoms, so that the requirement of coplanarity is here in force. Experimentally, Ley[2] found that the spectra of trans α-methyl stilbene and transα,α'dimethyl stilbene showed displacement of the long wave-length absorption peak of trans stilbene toward shorter wave-lengths by 300 A. and 600 A. respectively, because one of both the rings were turned from coplanarity with the ethylenic double bond by interference with the methyl groups. Also, Pickett, Walter and France[3] found that bimesityl and 2,2′,4,4′,6,6′ hexachlorbiphenyl absorb with thirty or forty-fold less intensity than biphenyl, because the non-coplanarity of the rings inhibits interaction between them.

EXPERIMENTAL

Absorption spectra of the compounds listed in the table below were

obtained, in hexane or cyclohexane solution, from 2330 A. to the upper wave-length limit of appreciable absorption. The apparatus consisted of a Bausch and Lomb medium quartz spectrograph, Bausch and Lomb sectorphotometer, and condensed spark between tungsten-steel electrodes. The cells were of fused quartz, five centimeters in length, with optically plane ends.

Twenty-one compounds, cases of steric hindrance preventing coplanarity of structure or related compounds for comparison, were studied. These compounds, with the chief features of their spectra, are listed in the following table:

	γ(max.)	ϵ(max.)
I. Biphenyl	2470 A.	17,000
II. 2,2′ dimethyl biphenyl	ϵ=6000 at 2337,	falls steadily
III. 3,3′ dimethyl biphenyl	2510	14,400
IV. 4,4′ dimethyl biphenyl	2540	21,100
V. 2,2′,4,4′ tetramethyl biphenyl	ϵ=10,500 at 2340,	falls steadily.
VI. Bimesityl	ϵ (min.)=400 at 2530	
	2670	600
VII. 3,3′ dimethoxy biphenyl	2520	12,000
	2870	6,000
VIII. 2,2′ dimethyl, 5,5′ dimethoxy biphenyl	ϵ (min.)=800 at 2540	
	2860	5,000
IX. 3,3′ (decamethylenedioxy) biphenyl	2530	12,000
	2850	5,000
X. 2,2′ dimethyl 5,5′ (decamethylenedioxy) biphenyl	ϵ (min.)=800 at 2570	
	2820	5,000
XI. 2,2′ dimethyl 5,5′ (octamethylenedioxy) biphenyl	ϵ (min.)=1000 at 2580	
	2830	5,000
XII. Acetophenone	2380	13,000
	2780	900

		γ(max.)	ϵ(max.)
XIII.	2,4 dimethylacetophenone	2470	13,000
		2850	1,200
XIV.	Acetomesitylene	ϵ=4000 at 2330, falls steadily	
XV.	2,4,6 triisopropylaceto-phenone	ϵ=3000 at 2337, falls steadily	
XVI.	Benzophenone	2650	13,000
XVII.	Benzoylmesitylene	2430	16,000
XVIII.	Dimesityl ketone	2470	20,000
XIX.	cis- 2,4,6,2′,4′,6′ hexaiso-propyl α,α'dihydroxy stil-bene diacetate	2500	20,000
XX.	trans- 2,4,6,2′,4′,6′ hexa-isopropyl α,α'dihydroxy stilbene diacetate	ϵ=24,000 at 2350, falls steadily and rapidly	
XXI.	cis- 2,4,6,2′,4′,6′ hexaiso-propyl α,α'dihydroxy stil-bene dimethyl ether	2580	12,000

DISCUSSION OF RESULTS

In biphenyls we expect para substituents to shift the absorption to longer wave-lengths by lowering the energy of the ionic form, with positive and negative charges at the opposite ends of the molecule, which is assumed to contribute largely to the upper state of the longest wave-length intense transition[4]. Meta substituents we assume to interact with the biphenyl system to give ionic excited states involving a single ring, which compete with the ionic state with charges in the para positions. We expect, therefore, a reduction of the intensity of absorption in the biphenyl peak and the appearance of a second peak arising from the competing transition. The spectra of IV, III, VII, and IX, show good correspondence with these ideas.

From ortho substituents we expect, in addition to electronic effects,

a steric effect arising from the spacial interference of ortho substituents with other ortho substituents or hydrogen atoms on the opposite ring, which forces the two rings out of coplanarity. The spectra of II, V, VI, VIII, X, XI show the great decrease in the intensity of absorption at the wave-length of the absorption maximum of biphenyl which is produced by two or four ortho methyl groups. Comparison of the spectra of VIII, X and XI with those of VII and IX reveals that the second peak is not affected greatly by hindrance and suggests the explanation in terms of interaction of the meta substituents with the individual rings. These spectra are definite evidence that the biphenyl system in X is not coplanar. If, as seems probable, the same is true of the dicarboxylic acid obtained by the oxidation of X, then the optical activity of the acid[5] is of the usual biphenyl type and is not to be attributed to the possibility of two orientations of the polymethylene chain with respect to a "trans" coplanar biphenyl structure.

The results for the series XII, XIII, XIV, and XV show that the intense absorption of XII at 2380 A., arising from conjugation of the carbonyl double bond with the ring, remains, somewhat shifted, in XIII, but is greatly reduced in XIV and still more so in XV. We may conclude that the degree of interference between an ortho methyl group and the carbonyl oxygen is insufficient to turn the aceto group from coplanarity, while that between a second ortho methyl or isopropyl group and the ketone methyl group does turn the aceto group through a large angle. Scale diagrams yield predictions in good agreement with these conclusions.

The wave-lengths and intensities of the maxima for XVI, XVII and XVIII indicate that the carbonyl double bond is conjugated with at least one ring in all three compounds, and probably with the entire ring system in XVI. Diagrams to scale reveal a possibility of forms of XVII and XVIII with the carbonyl bond nearly in the plane of one ring.

The spectra of the substituted stilbenes show absorption at much shorter wave-lengths and lower intensities than is found for cis and trans stilbene themselves. The cis compounds absorb strongly at longer wave-lengths than the trans compound. The spectra of the cis compounds suggest at least partial conjugation of the ethylenic bond with one ring, while the spectrum of the trans compound suggests that both rings are forced far from coplanarity with the ethylenic bond.

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VITA

The writer was born August 22, 1913, in New York City. He attended elementary school in Hempstead, Long Island, N. Y., Burlington, N. J., and Miami, Florida, and received his secondary education in the Miami Senior High School. He attended the University of Florida at Gainesville, from 1930 to 1934 and received the A.B. degree in June, 1934. From 1934 to 1936 he held a Knights of Columbus Fellowship in the Graduate School of The Catholic University of America, Washington, D. C., and received the M.S. degree in biochemistry. During the year 1936-37 he held an instructorship in chemistry in the College of Notre Dame of Maryland in Baltimore. He entered the University of Illinois Graduate School in September, 1937. He held an assistantship in physical chemistry for the years 1937-38 and 1938-39, and a University Fellowship for the year 1939-40. He is a member of Phi Kappa Phi and Sigma Xi.